A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin

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ABSTRACT

The conversion of biomass by thermochemical means is very promising for the substitution of fossil materials in many energy applications. Given the complexity of biomass the main challenge in its use is to obtain products with high yield and purity. For a better understanding of biomass thermochemical conversion, many authors have studied in TG analyzer or at bed scale the individual pyrolysis of its main constituents (i.e. cellulose, hemicelluloses and lignin). Based on these studies, this original work synthesizes the main steps of conversion and the composition of the products obtained from each constituent. Pyrolysis conversion can be described as the superposition of three main pathways (char formation, depolymerization and fragmentation) and secondary reactions. Lignin, which is composed of many benzene rings, gives the highest char yield and its depolymerization leads to various phenols. The depolymerization of the polysaccharides is a source of anhydro-saccharides and furan compounds. The fragmentation of the different constituents and the secondary reactions produce CO, CO_2 and small chain compounds. For temperature higher than 500 °C, the residues obtained from the different constituents present a similar structure, which evolves towards a more condensed polyaromatic form by releasing CH_4, CO and H_2. As the aromatic rings and their substituent composition have a critical influence on the reactivity of pyrolysis products, a particular attention has been given to their formation. Some mechanisms are proposed to explain the formation of the main products. From the results of this study it is possible to predict the reactivity and energy content of the pyrolysis products and evaluate their potential use as biofuels in renewable applications.

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1. Introduction

A massive growth of fossil feedstock consumption accompanied the industrial revolution; but faced with the depletion of fossil resources and the impact of their use on the environment, alternative raw materials must be found. As the precursor of fossil feedstocks, biomass is also composed of carbon and appears to be one of the best renewable solutions for the substitution of fossil resources in many applications. Indeed, biomass can be used in energy applications for the production of heat, power and transportation fuels [1]. The production of chemicals (food additives, pharmaceuticals, surfactants, organic solvents, fertilizers) and biomaterials from biomass is also becoming more and more common [2]. The use of biomass for these applications generally requires multi-step conversions of the raw material. In order to develop more competitive processes, a valorization of the entire content of biomass in biorefineries inspired by the model of those exploited for petroleum products constitutes one of the key issues [3].

Among the processes of biomass valorization, its conversion by thermochemical means appears to be a promising alternative for many energy applications [1]. The most current thermochemical processes (which consist of a conversion of the biomass by the action of heat) are gasification, pyrolysis and combustion. However in some of these applications, further research is still needed to improve the purity of intermediate and final products. For instance, the development of the production of synthetic hydrocarbons by gasification and the Fischer–Tropsch process is hindered by overly high contaminant content in the gas produced by biomass gasification [4]. In the case of the production of bio-oil by flash pyrolysis, the oxygen content of the obtained product is generally too high for the substitution of conventional petroleum fuels [1,5]. As a consequence, additional upgrading steps, which dramatically affect the energy efficiency of the process, are frequently necessary to improve the purity of the products. That is why the development of the valorization of biomass by thermochemical means requires a better control of biomass conversion.

Pyrolysis is a capital step of biomass thermochemical conversion as it is the first step of all the processes. Pyrolysis consists in the conversion of biomass by the action of heat in an inert atmosphere into char, gas and a liquid composed of a mixture of hundreds of oxygenated organic compounds [6,7]. Depending on the operating conditions, an important variety of products and yields can be obtained [1,5]. Besides, the diversity in the composition of biomass which is constituted by three main polymers (i.e. cellulose, hemicelluloses and lignin) also contributes to the complexity of the final product. Many authors studied the influence of operating conditions on products yields [1,5,8]. For instance, it is widely accepted that a high heating rate favors the formation of volatile compounds whereas a low heating rate promotes the production of char [1,5]. However, owing to the complexity of biomass conversion, few authors tried to explain the influence of pyrolysis conditions on the chemical reactions involved at the molecular scale and sometimes different names are used for similar mechanisms [8,9]. From the literature, it appears that the pyrolysis of biomass is most frequently considered as the superposition of three main primary mechanisms (i.e. char formation,
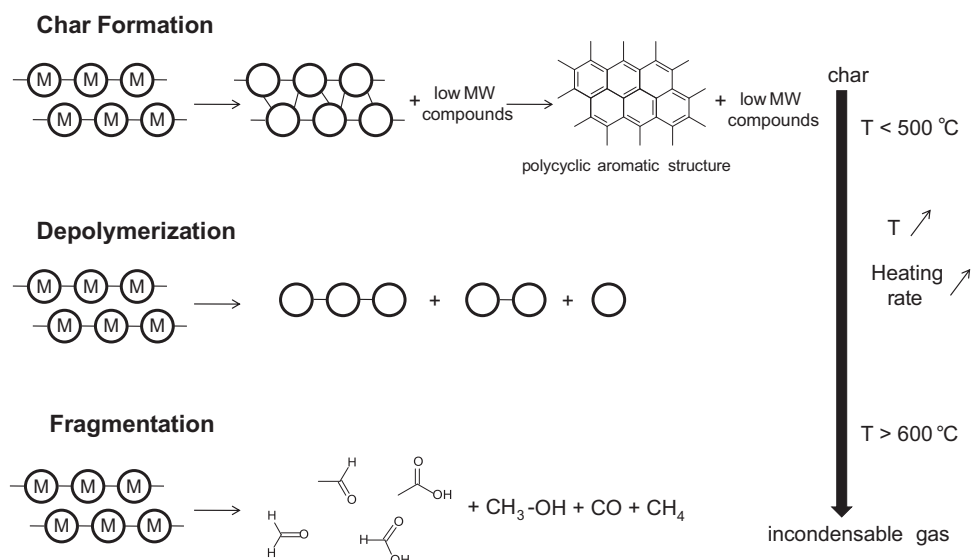

Fig. 1. Pathways involved in the primary mechanisms of the conversion of biomass constituents (M: monomer; MW: molecular weight).

depolymerization and fragmentation) and of secondary mechanisms [8,10–12]. For a better understanding of these mechanisms, based on a review of the published research works, we proposed a precise description of these mechanisms, suitable whatever the considered constituent. Then, the influence of the operatory conditions on the preponderance of the mechanisms is discussed.

Given the complexity of biomass pyrolysis conversion and the diversity of the obtained products, it may be more convenient to study separately the conversion of each constituent. Several authors have analyzed the composition of the products resulting from the individual pyrolysis of cellulose [10,13,14], hemicelluloses [15–17] and lignin [18–20]. For a same constituent, significant differences in the product yields can be found, because of the variety in the origin of the constituent and of the operatory conditions imposed. With the heating rate, the particle size of the material and the gas residence time, the temperature of the reactor is naturally one of the most important parameters that affect the yields [1,21]. This work provides a state of the art of the influence of the temperature conditions on the formation of the products obtained from the individual pyrolysis of biomass constituents. The goal is, for each of the main reactions involved in biomass conversion, to evaluate the required temperature to enable these reactions. To this aim, for each biomass constituent, a collection and a comparison of the published results of many experiments of pyrolysis in different kinds of reactors was undertaken. In certain cases, based on the evolution of the structure of the products we propose some mechanisms to explain such evolutions. The formation of aromatic rings and in particular benzene rings is a critical step of the conversion. On the one hand because benzene rings are the units which constitute the char residue; the rate at which they are formed and they combine together significantly influences the char yields. On the other hand because whatever the considered application (combustion, pyrolysis or gasification) the composition of the substituents of the benzene rings will influence the reactivity of the intermediary products (char and volatiles) and thus the operatory conditions of the following steps of the process. In particular the formation and conversion of very stable phenols [22] is a critical issue in many applications. In gasification process the formation of these compounds limits the conversion efficiency and causes fouling on process equipment surfaces [4]. Moreover when catalysts are used, phenols condensation is responsible for the catalyst deactivation [23]. Such issues limit the development of high-impact projects such as the production of diesel fuel from biomass by gasification and Fischer–Tropsch synthesis. In the case of fast pyrolysis, many works have been focused on the deoxygenation of the phenols in order to upgrade the bio-oil [22]. In this work, for each constituent a particular attention has been paid to the formation of the aromatic rings and to their substituent composition. The database provided by this review can constitute a useful tool to explain the composition of the obtained products or to optimize biomass pyrolysis yields. Finally, it is worth noting that pyrolysis mechanisms can be influenced by interactions between polymer constituents and with minerals present in biomass [24–26]. The effect of these interactions on product distribution is discussed in the last section.

2. Mechanisms of conversion of biomass constituents by pyrolysis

During the heating of biomass, different chemical bonds within the polymers are broken, which results in the release of volatile compounds and in rearrangement reactions within the matrix of the residue. These reactions are considered as primary mechanisms [8,16]. Then, after their formation, some volatile compounds are unstable and can undergo additional conversions named secondary reactions.

2.1. Primary mechanisms

The main biomass constituents are biopolymers. According to the literature, their primary conversion present common characteristics and can be described by three main pathways, depending on the nature of the chemical bonds that are broken. Most frequent terms used to characterize these pathways, which are presented in Fig. 1, are char formation [27–29], depolymerization [8,9,30] and fragmentation [8,14,30].

2.1.1. Char formation

Char formation consists in the conversion of biomass in a solid residue named char which presents an aromatic polycyclic structure [31,32]. This pathway is generally favored by intra- and intermolecular rearrangement reactions, which result in a higher degree of reticulation and in a higher thermal stability of the residue [31,33]. The main steps of this pathway are the formation of benzene rings and the combination of these rings in a polycyclic structure. All these rearrangement reactions are generally accompanied by the release of water or incondensable gas [8,30,33,34].

2.1.2. Depolymerization

Depolymerization consists in the breaking of the bonds between the monomer units of the polymers. After each rupture, stabilization reactions of the two new chain ends occur [9,33]. Depolymerization results in a decrease in the degree of polymerization of the chains until the produced molecules become volatile [9,35,36]. These molecules, which are condensable at ambient temperature, are most frequently found in the liquid fraction in the form of derived-monomer, dimer or trimer [6,37].

2.1.3. Fragmentation

Fragmentation consists in the linkage of many covalent bonds of the polymer, even within the monomer units [8,14], and results in the formation of incondensable gas and of a diversity of small chain organic compounds which are condensable at ambient temperature [8,38,39].

2.2. Secondary mechanisms

When the released volatile compounds are not stable under the conditions of reactor temperature, they can undergo secondary reactions such as cracking [8,40] or recombination [40,41]. Cracking reactions consist in the breaking of chemical bonds within the volatile compounds, which result in the formation of lower MW (molecular weight) molecules [7,21]. As the breaking of the same chemical bonds can undergo either within the polymer or within the volatile compounds, there are similarities in the products obtained from the fragmentation and cracking reactions [39] and sometimes it is difficult to appreciate which pathway is mainly responsible of the formation of the low MW compounds. Recombination (or recondensation) consists in the combination of volatile compounds to give a higher MW molecule, which sometimes is no longer volatile under the conditions of temperature of the reactor [16,40]. When the recombination happens inside the pores of the polymer, this reaction can lead to the formation of a secondary char [21,41]. In gas phase, the presence of PAH is characteristic of favorable conditions for recombination reactions [40]. Secondary mechanisms can be catalyzed at the surface of the char, of the reactor or of eventual added catalysts. In the case of recombination, these reactions can lead to the formation of a deposit on the catalytic surface [40].

2.3. Influence of pyrolysis conditions on the potential pathways

It is well accepted that the distribution of char and volatile yields is very dependent on the heating rate of the polymers [1,5]. With low heating rates (< 10 °C/min), when the weakest chemical bonds break, many others are still stable, so that the structure of the polymer is just slightly affected, which favors rearrangement reactions to give a more stable matrix [21,42] and thereafter inhibits the formation of volatile compounds. With very high heating rates (> 100 °C/s), many types of chemical bonds are simultaneously broken, which leads to the release of many volatile compounds, before rearrangement reactions are likely to happen. Particle size of the feedstock is directly related to the heating rate of the solid fuel. Several works have demonstrated that the yield of volatiles increases with particle size decrease, especially in the case of fine particles (< 1 mm) [21,42].

The distribution of volatile compounds highly depends on the temperature of the reactor. While depolymerization reactions essentially undergo between 250 °C and 500 °C [8,21], fragmentation reactions on this temperature range only concern a few types of chemical bonds [8]. As a consequence optimum liquid yields are obtained in processes where the temperature of the reactor is

generally comprised between 450 °C and 550 °C [5,21]. With the rising of the temperature of the reactor above 550 °C, more and more fragmentation reactions happen, which results in the formation of low MW compounds, some of which are incondensable [8]. Concerning secondary reactions, specific works have shown that the influence of the cracking of volatile compounds on product yields become significant for temperature above 600 °C [7,40,43], while the appearance of PAH, characteristic of recombination reactions, is generally observed at much higher temperatures (≥ 800 °C) [17,40]. These secondary reactions are more likely to happen when the residence time of the volatile compounds in the reactor is long [41,43].

3. Individual conversion of the main biomass constituents

In this part, the pyrolysis of each of the main biomass constituents is individually discussed. First, the results from literature concerning thermogravimetric (TG) analysis are used to detail the main steps of conversion. The curve representing the mass loss rate of a constituent generally presents a similar profile with a unique main peak, as illustrated in Fig. 2. Depending on the step of conversion, different types of reactions are predominant. At the beginning of the pyrolysis, after the loss of the moisture, the mass decrease is due to the conversion of the most unstable functions by rearrangement or fragmentation reactions. It is generally well accepted that the maximum weight loss rate corresponds to the conversion stage where the depolymerization rate of the constituent is the highest [19,44]. For higher temperatures, the charring process which consists in the organization of the benzene rings in a polycyclic structure takes place. The mass loss is progressive and most of the released compounds are incondensable gases with low MW [8,45]. In TG analysis, it is well known that the characteristic temperatures (i.e. onset, peak and offset temperatures of the maximum weight loss rate) depend on the heating rate. Studies realized with a low heating rate (≤ 20 °C/

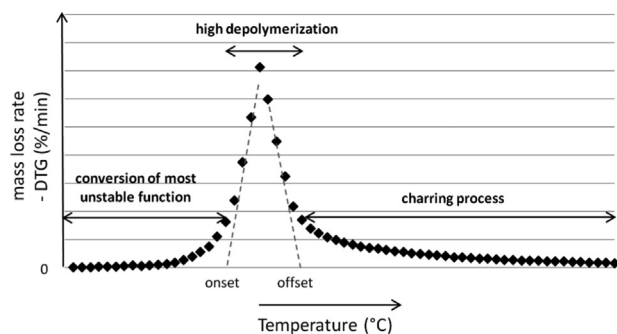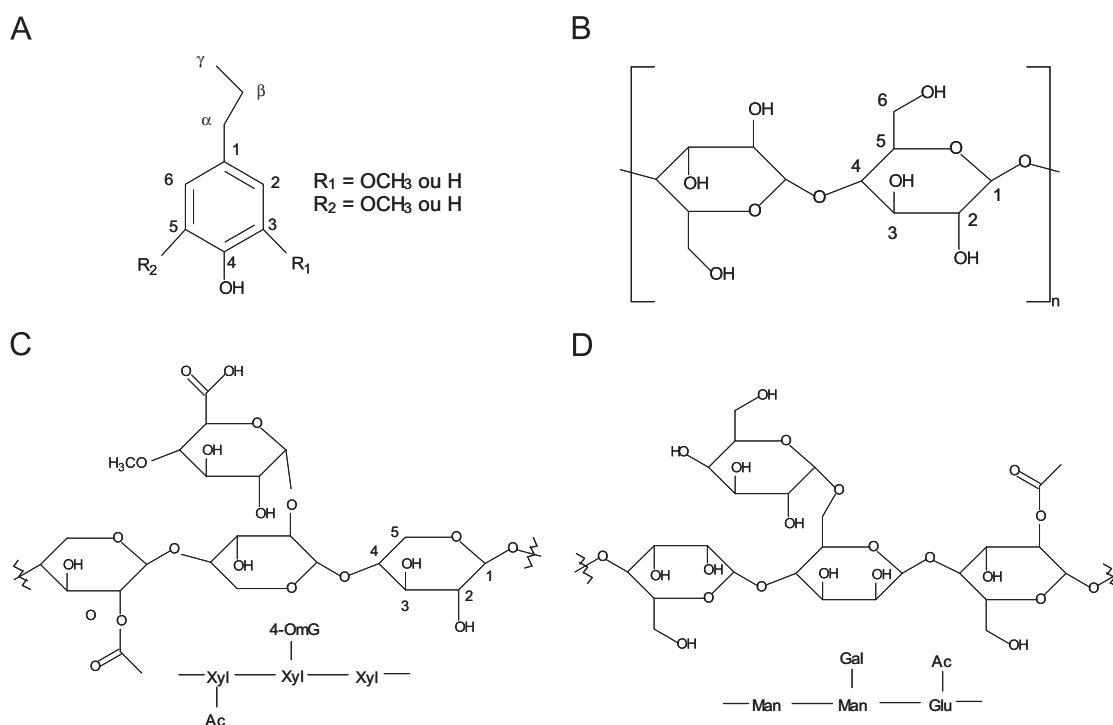**Fig. 2.** TG analysis of the main steps of conversion of biomass constituents.

Fig. 3. Chemical structures of biomass constituents. (A) Building units of lignin; (B) building units of cellulose; (C) partial structure of xylan; and (D) partial structure of glucomannan (Xyl: xylopyranose, 4-OmG: 4-O-methylglucuronic acid, Man: mannopyranose, Glu: glucopyranose, Gal: galactopyranose, Ac: acetyl).

min) will be privileged to determine more precisely the temperatures from which the pyrolytic reactions start.

In order to study the yield and composition of the products, the pyrolysis of biomass constituents has been studied at the bed scale in various types of reactor (fixed bed, fluid bed, ablative, rotating cone, auger, vacuum) at laboratory- and pilot-scale [46–48]. The choice of the technology which depends on the application influences many parameters such as the particle size of the feedstock, the heat transfer rate, the residence time of the solid and volatiles. The advantages of each technology and the influence on pyrolysis yields are discussed in several reviews [46–48]. The composition of the gaseous fraction (CO_2, CO, CH_4, H_2) is analyzed by GC [10,13,30,49]. Concerning the pyrolysis oil, its water content is generally determined by Karl–Fischer titration [10,30,50] and the composition of the main organic compounds can be analyzed by GC/MS [13,14,16,17,30]. Given the complexity and the relatively high MW of the derived-oligomers present in the oil, these compounds cannot be analyzed by GC and gel permeation chromatography is sometimes used to determine the MW distribution [16]. These analytical results give information about the reactions occurring for temperature less than or equal to the one of the reactor. In fact it is not really possible to determine precisely the temperature of the formation of the different products, as most of the volatile compounds are released before the temperature of the sample reaches the temperature of the reactor. Study of conversions realized at the bed scale with high heating rates also give information about the influence of secondary reactions on volatile composition. In this work we study the reactions occurring for pyrolysis temperature below 800 °C therefore the secondary reactions will essentially be cracking reactions.

More precise information about conversion mechanisms is provided by coupling TG analysis and an on-line analyzer of the evolved products such as MS [25,51,52] or FTIR [13,49,53]. With this approach, it is possible to study the composition of the evolved products throughout the temperature rise of the sample. Given that structures of the depolymerization products are very close to the one of the units within the residue, these couplings help to understand the evolution of the composition of the sample. Besides, the study of the evolved compounds provides information about the temperature of reactions of fragmentation of unstable functions at the beginning of the conversion and of rearrangement during the charring process. Moreover, additional information can be provided by analyses by FTIR, XRD or NMR of the chemical changes occurring in the solid residue prepared by pyrolysis performed with different temperatures [32,47,54,55].

Based on a review of the experiments of individual pyrolysis of the main biomass constituents, we explicit thereafter the mechanisms involved during the main steps of the conversion of each constituent and describe the composition of the products obtained by each mechanism. Discussed mechanisms occur between 150 °C and 800 °C, after the evolution of the moisture. It is worth noting that by thermochemical conversion, some steps are sometimes described by ionic reactions [14,55,56], but in many cases, especially for the conversion of lignin, the authors generally propose radical reactions to explain the different evolutions [19,27,57,58].

3.1. Lignin conversion

3.1.1. Description of lignin structure

Lignin is a complex three-dimensional amorphous polymer composed of three phenylpropane units: p-hydroxyphenyl (H), guaicyl (G) and syringyl (S). The proportions of the monomer units are highly variable and mainly depend on the lignocellulosic
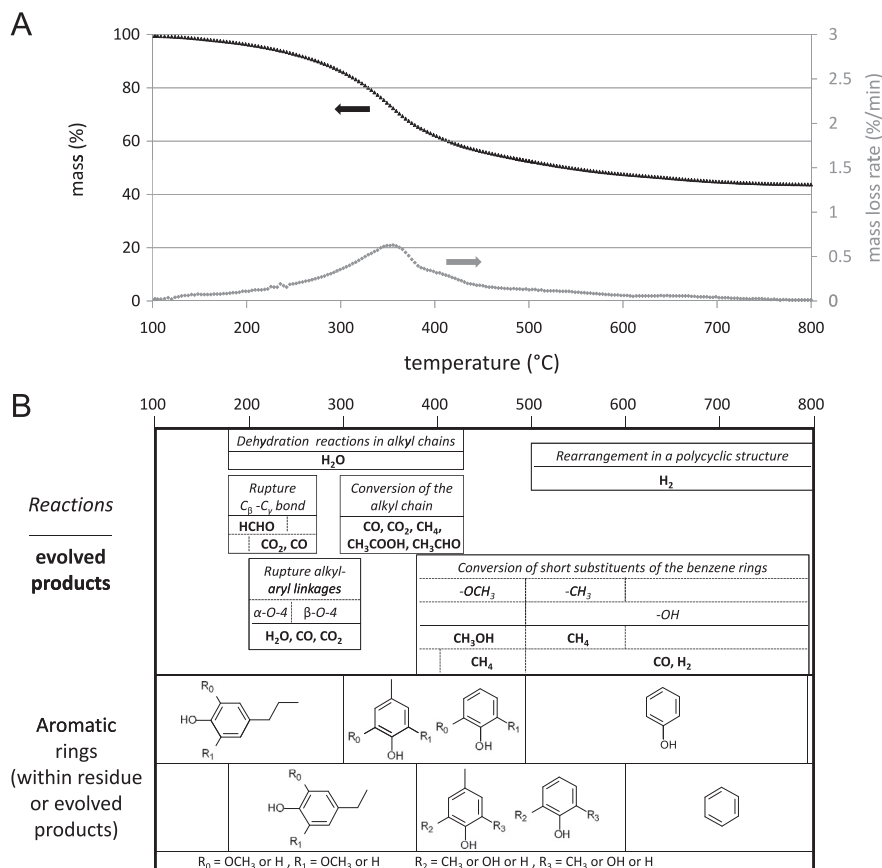
Fig. 4. Lignin pyrolysis: (A) Typical TG analysis (2 °C/min adapted from [23]), and (B) main reactions occuring and evolution of the chemical structures of the aromatic rings (within the residue and the evolved products) throughout the temperature increase.

species. These units, which contain a hydroxyl group in para position of the alkyl chain, differ in the degree of methoxylation of the aromatic ring as illustrated in Fig. 3A. The units are connected by different ether and carbon to carbon linkages. The most common are β-O-4, 4-O-5, α-O-4, β–β, β-5, β-1, 5-5 [59,60]. In addition to the ether functions created during lignin biosynthesis, the alkyl chains also contain other oxygenated groups such as alcohol, carbonyl and carboxylic acid functions [38,61].

3.1.2. The mechanism of lignin conversion

A typical thermogram obtained from TG analysis of lignin is presented in Fig. 4A. Given the variety of the chemical functions which differ in thermal stability, the main conversion step of lignin occurs over a large temperature range from 200 to 450 °C, with a highest decomposition rate generally comprised between 360 and 400 °C [61–63]. The reactions responsible of the release of volatile compounds are mostly due to the instability of the propyl chains, of some linkages between monomer units and of the methoxy substituents of the aromatic rings. After this step, responsible of the main release of primary volatiles, a charring process which consists in the rearrangement of the char skeleton in a polycyclic aromatic structure occurs. The volatile compounds released by these rearrangement reactions are mostly low-weight incondensable gases [45,64].

Under inert atmosphere, benzene rings are very stable and their concentration within the residue tends to increase throughout the reaction [54,65,66]. Given that most of the aromatic rings which will form the char are already present in the initial lignin, it is easier to understand the phenomena occurring during the charring process of lignin than during the ones of the polysaccharides. That is why we first present the mechanisms of conversion of lignin. The main steps of conversion of lignin and the light volatile compounds released during each step are detailed thereafter and illustrated in Fig. 4B. The evolution with the temperature rise of the composition of the substituents of the aromatic rings is also investigated. This information allows following the change in structure of the aromatic rings within the residue, but also of those of the aromatic volatile compounds likely to be released on this temperature range.

3.1.2.1. Conversion of the alkyl chains and rupture of some of the linkages between units (150–420 °C).
The conversion of the propyl chain begins at 180 °C [38,61]. Its hydroxyl groups are implied in dehydration reactions [38,62]. When the hydroxyl group is located on the carbon C_γ, a fragmentation between the atoms C_β and C_γ, which provokes the release of formaldehyde, is also frequent [38,45]. When the carbon C_γ is implied in carbonyl or carboxyl functions, the same reaction is likely to occur, at temperatures slightly higher, and leads to the formation of CO and CO_2 respectively [38,61,62,64]. Regarding the chemical bonds linking the monomer units, the ether linkages involving the alkyl chains are supposed to be the less stable. The linkage α-O-4 can react at 200 °C [67]. The most common linkage in lignin, β-O-4 [59,68], can be broken when the temperature reaches 245 °C [57,67]. The reorganization of the chemical groups formed by the breaking of these ether bonds, can lead to the formation of oxygenated compounds such as CO, CO_2 and H_2O [63,64]. Besides, the breaking of bonds between monomer units can also provoke the release of phenolic compounds (monomers or oligomers) with a structure close to the one of monomer units, that is to say with an alkyl chain composed of 2 or 3 atoms of carbon (4-vinylguaiacol, eugenol) [18,19,56,61,66].

For higher temperatures ($T > 300$ °C), most of the C–C bonds within and between the alkyl chains become unstable and react, which is proven by the decrease in concentration of aliphatic

groups within the residue [54]. Besides the small chain compounds already released during previous steps, other compounds containing 1–3 atoms of carbon such as CH_4, acetaldehyde or acetic acid can be formed [56,64]. As a consequence, most of the phenolic compounds released on this temperature range are characterized by a methyl group in the position 1 (p-cresol) or even an absence of alkyl chain in this position (guaiacol, syringol) [17,26,63]. These reactions, which provoke the rupture of many of the ramifications between the aromatic rings, are responsible of the highest decomposition rate of the lignin (360–400 °C) and of the maximum rate of production of phenols [18,63].

3.1.2.2. Conversion of the short substituents of the aromatic rings and charring process (380–800 °C).
The methoxy groups in ortho position of the hydroxyl group become reactive when the temperature reaches 380 °C [61,69]. Different types of reactions of fragmentation result in the substitution of the methoxy group by –OH, –CH_3 or –H group [61,69,70]. At 400 °C, the fragmentation of the methoxy groups leads to an important formation of methanol [18,38,45]. At 430 °C, the methoxy groups are also the source of CH_4 production [38,45,71]. These two fragmentation reactions, which are supposed to happen following a homolytic cleavage explain the formation of new –H or –OH substituent respectively [27,61], as illustrated in Fig. 5A and B. On the other side, it is more complex to explain the formation of –CH_3 groups at the same position. This reaction could occur following a mechanism involving an o-quinonemethide intermediary and be responsible of the formation of H_2O [27,69]. All these reactions of the methoxy group in the ortho position of the hydroxyl group require the involvement of hydrogen donor groups. Some of the hydrogen atoms could be brought by H_2 molecules [61], but it is not evident that these molecules are already formed on the temperature range corresponding to the methoxy conversion. The hydrogen atom may also be given by another aromatic ring as illustrated in Fig. 5C. In this case, the conversion of the methoxy would result in a higher reticulation of the residue.

For temperature higher than 450 °C, most of the initial bonds between monomer units have been broken. Only the more stable such as the phenyl linkage 5-5 and the ether linkage 4-O-5 are still present [67,72]. The main short substituents of the aromatic rings are –CH_3 or –OH. The char becomes more and more aromatic and most of the evolved compounds are incondensable gases. FTIR analyses show that the –CH_3 substituents disappear between 500 and 600 °C [54], while the studies of the evolution of the evolved compounds generally show a local maximum of CH_4 formation rate between 550 and 580 °C [18,38,45,63]. As a consequence, it is probable that the CH_4 is released according to a mechanism of demethylation [71] as shown in Fig. 5D, which leads to a more reticulated structure.

Many authors have found that the pyrolysis of lignin releases an important amount of CO between 500 and 800 °C [18,38,45,63]. The curve representing the production of CO as a function of the temperature is generally composed of several local maxima. Depending on the studies, the temperature of these maxima can differ, certainly because of differences in the origin of the lignin and in the method used for their extraction. Given that on this temperature range, very few condensable organic compounds are released, the production of CO is not likely to be due to secondary reactions of these compounds, but to the conversion of some oxygenated groups still present in the residue. The oxygenated functions remaining in the residue are the ether linkage 4-O-5 and the hydroxyl substituents. The rupture of the ether bonds 4-O-5 is effectively supposed to be a source of production of CO [45,63]. The first step of the conversion could be due to a hydrogenation of the ether bond, leading to the formation of an additional hydroxyl substituent [73], which will then react. According to the literature
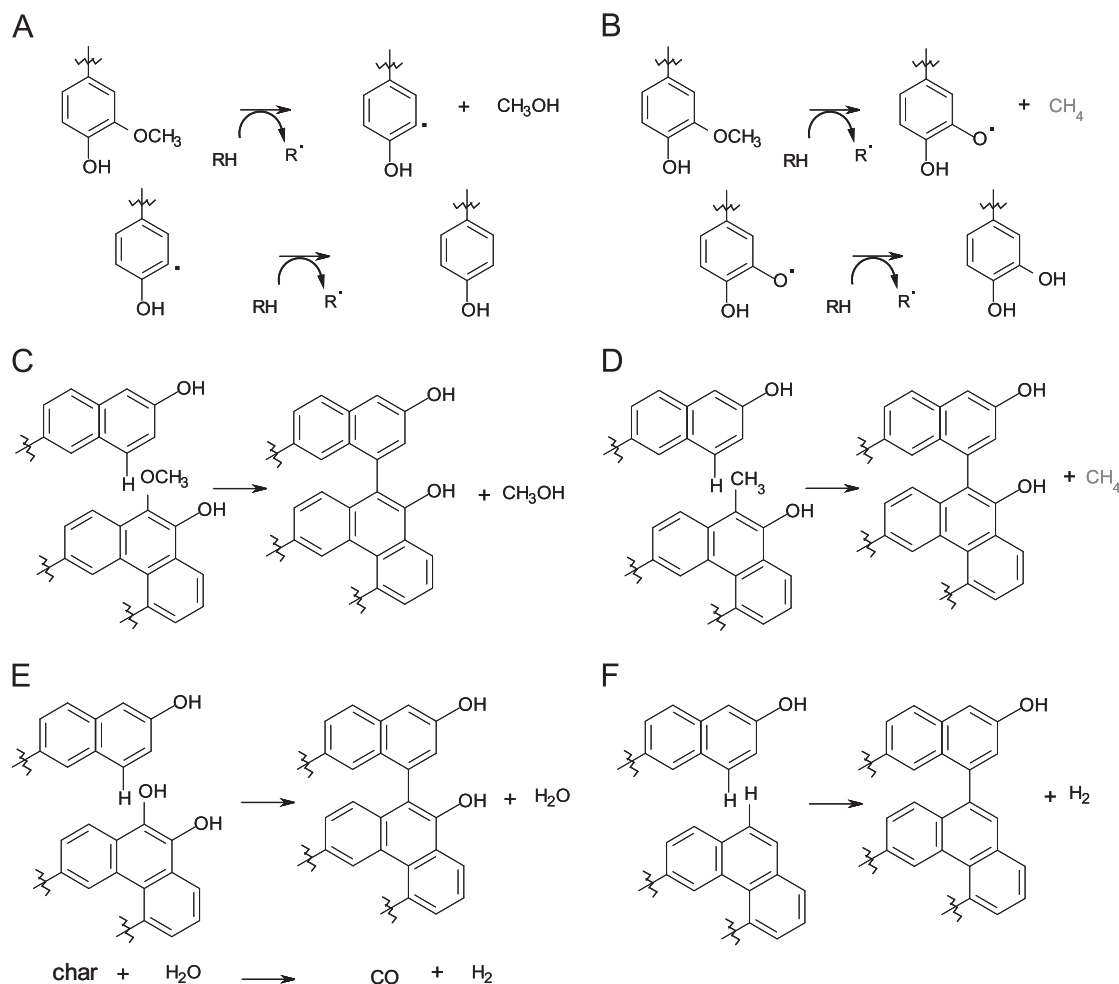
Fig. 5. Mechanisms of conversion of the substituents of the benzene rings.

[70,74], when located in ortho position of an hydroxyl substitutient, an hydroxyl group is more reactive than a methyl group (which is converted between 500 and 600 °C), therefore some of the hydroxyl groups are certainly converted before 600 °C [74]. The formation of CO for higher temperatures is certainly due to the conversion of the phenol rings (which contain a unique hydroxyl substituent) of the residue, which are known to still be stable at 550 °C [54,74]. Very few authors have proposed a mechanism to explain the formation of CO from the conversion of the phenol rings: Asmadi et al. [74] suggested a mechanism but only from a pyrogallol moiety (derived from S unit) and Eggsgard et al. [75] detailed a relatively complex mechanism which requires two phenol moieties. In these two mechanisms, one step consists in the conversion or the rupture of a very stable benzene ring. Based on the mechanism involving methyl substitutions proposed Fig. 5D, it seems possible that the same kind of reaction could happen with hydroxyl substituent (Fig. 5E). This reaction could lead to the formation of H_2O molecules inside the particles, which could immediately react with the char by vapogasification to give CO and H_2. As a consequence of the reactions involving the last oxygenated organic groups, for conversion with temperatures higher than 800 °C, most of the aromatic rings of the volatile compounds and of the residue are deoxygenated [17,54]. Finally, a production of H_2 is due to the rearrangement of the aromatic rings in a polycyclic structure [64,69], following a mechanism as presented in Fig. 5E. This reaction is highlighted by the important amount of evolved H_2 for temperatures higher than 500 °C [49,76].

3.2. Cellulose conversion

3.2.1. Description of cellulose structure

Cellulose is a linear homopolysaccharide of cellobiose monomers, composed of two β-glucopyranose units as presented in Fig. 3B. All the covalent linkages between the β-glucopyranose motifs of the framework are β-1,4-glycosidic bonds. The degree of polymerization of the native cellulose depends on the source and can reach more than 5000 [68]. The frequent intermolecular hydrogen bonds within the cellulose matrix result in a similar orientation of most of the molecules to form microfibrils. Depending on the degree of organization of its structure, cellulose is composed of crystalline (highly ordered) and amorphous (randomly distributed) phases [13].

3.2.2. Mechanism of cellulose conversion

A typical thermogram obtained from TG analysis of cellulose is presented in Fig. 6A. After a very little weight change from the start of temperature rise to 300 °C, the main conversion of cellulose occurs between 300 and 390 °C with a highest decomposition rate generally comprised between 330 and 370 °C [25,49,51]. During this step, most of the evolved products are condensable organic compounds. The total yield of these compounds can reach more than 70% in weight [10,16]. For temperature higher than 400 °C, the residue becomes more and more aromatic [31]. The main steps of conversion of cellulose and the volatile compounds released during
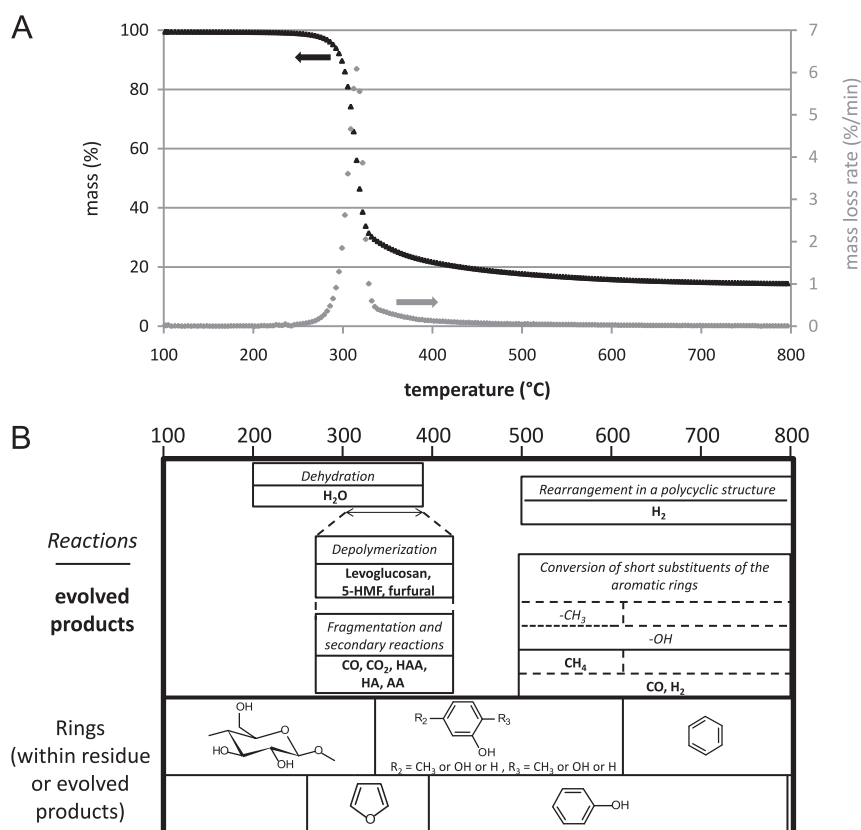
Fig. 6. Cellulose pyrolysis: (A) Typical TG analysis (2 °C/min adapted from [23]); and (B) main reactions occuring and evolution of the chemical structures of the rings (within the residue and the evolved products) throughout the temperature increase; HAA: hydroxyacetaldehyde, HA: hydroxyacetone, and AA: acetaldehyde.

each step are detailed thereafter and illustrated in Fig. 6B. The evolution of the chemical structure of the rings is also investigated.

3.2.2.1. Formation of the active cellulose or anhydrocellulose (150–300 °C). During the small mass loss before 300 °C, different reactions occur and can lead to the formation of an intermediary sometimes called active cellulose or anhydrocellulose [8,33,34]. The term active cellulose generally refers to an intermediary resulting from a partial depolymerization of the cellulose [29,77], whereas anhydrocellulose rather consists in an intermediary formed after dehydration reactions [33]. From a comprehensive analysis of works on cellulose pyrolysis it appears that, whatever the name of the intermediary formed, this one results of both reactions, with a preponderance which depends on the heating rate of the conversion.

Dehydration reactions are certainly responsible of most of the weight loss of the cellulose before 300 °C. While H_2O molecules are already released from a cellulose heated at 200 °C [25,33], CO, CO_2 and organic compounds are rarely detected in the volatile phase before 280 °C [25,49]. It is well accepted that dehydration reactions are highly correlated with char yields. Dehydration reactions can be intermolecular (between two chains) or intramolecular (within a glucopyranose moiety) [33]. Intermolecular dehydration can result in the formation of additional covalent bonds, leading to a higher reticulation and thermal stability of the polymer. Intramolecular dehydration leads to the formation of C=C double bonds, which can promote the formation of the benzene rings composing the char. In the beginning of cellulose conversion, it seems that dehydration reactions are mostly intermolecular. Indeed, after the heating at 250 °C of a cellulose during 5 h, most of the H_2O molecules formed came from intermolecular reactions and only one glucopyranose unit out of 30 contained a C=C double bond [33].

Although being relatively slow, depolymerization reactions are also possible before 300 °C. Depolymerization is due to the rupture of the glycosidic linkages (transglycosylation) between the monomer units and, when complete, leads to the formation of levoglucosan (LG). According to Mamleev et al. estimations [9], the elimination of the LG-end of a chain requires on average 22 h at 260 °C and 42 min at 305 °C. Moreover, given that H_2O can catalyze the transglycosylation, these times are certainly shortened in presence of the molecules formed from dehydration reactions. The possibility of a progressive depolymerization of cellulose is proven by different authors who isolated an intermediary composed of a mix of oligomers [35,50,55].

It is well known that the higher char yields produced from the pyrolysis of cellulose are obtained with slow heating rates [13]. Indeed, in such conditions, some dehydration reactions occur before the beginning of the depolymerization reactions and stabilize the cellulose matrix. In the contrary, with high heating rates, the depolymerization reactions are very fast and cellulose is quickly converted into volatile compounds, before any significant stabilization of the matrix. The loss of crystallinity of the cellulose, happening between 270 °C and 300 °C [32,55], also contributes to its high reactivity for higher temperatures.

3.2.2.2. Depolymerization (300–390 °C). For temperatures higher than 300 °C, the glycosidic bond becomes very reactive [77] and many reactions occur simultaneously. Cellulose depolymerization is very fast and its conversion can yield to more than 80% of volatile compounds which are mostly condensable organic compounds [13,25,26,49]. The depolymerization of cellulose leads to the formation of a high proportion of anhydro-oligosaccharides and anhydro-saccharides [10,14,78], especially of levoglucosan (1,6-anhydro-β-D-glucopyranose, $C_6H_{10}O_5$) whose yield can reach up to
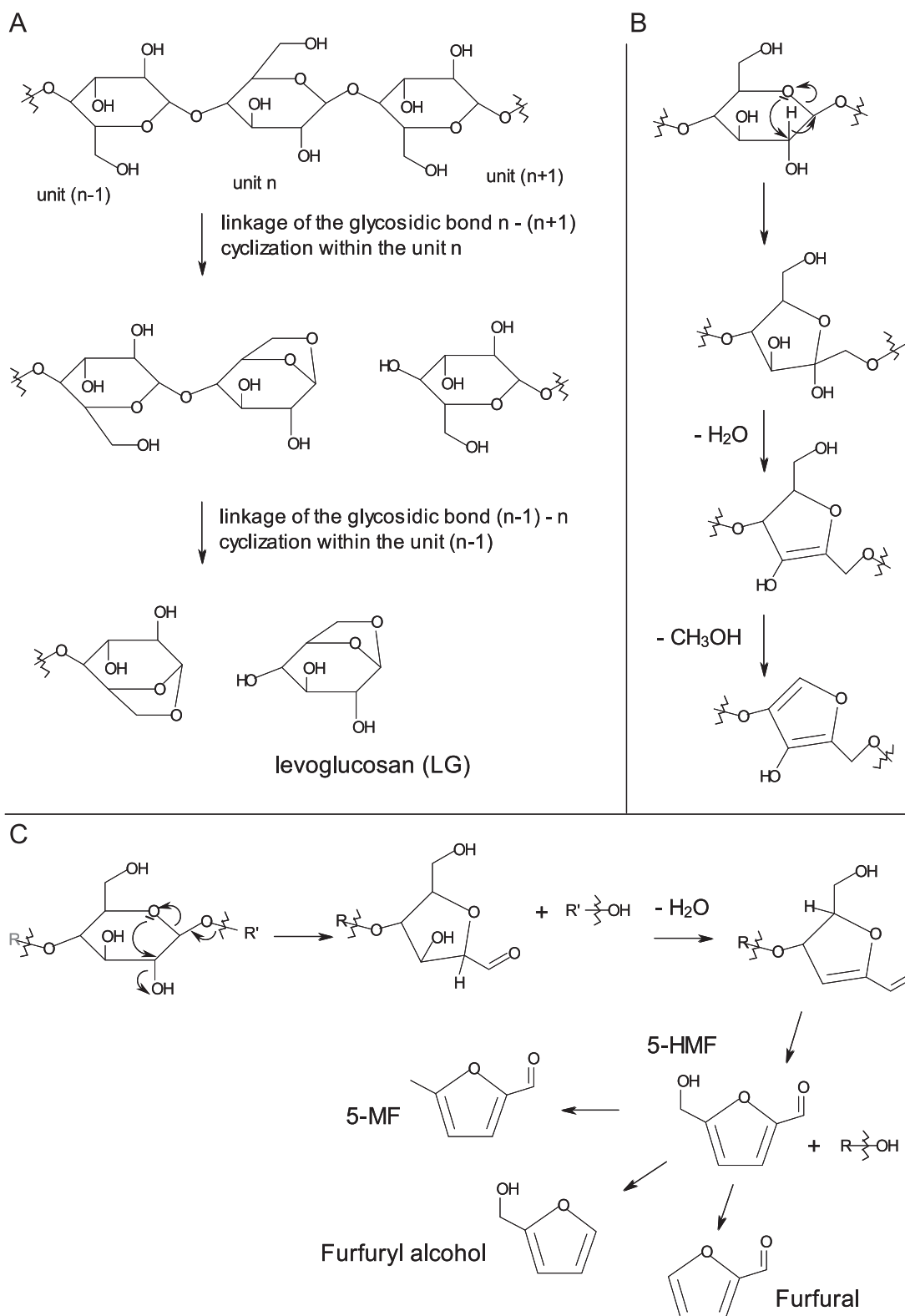
Fig. 7. Conversion of cellulose, proposed pathways for the formation of levoglucosan (A), furan rings within the residue (B) and volatile furan compounds (C).

60% [10,25] and of levoglucosenone ($C_6H_6O_3$) [12,14]. Different authors have proposed ionic or radical mechanisms to explain the formation of levoglucosan [13,14,33]. Whatever the type of mechanism proposed, it appears that a new ring is formed by a cyclization between the atom of carbon C_1 and the atom of oxygen of the hydroxyl group attached to the atom C_6, as illustrated in Fig. 7A.

The other anhydro-saccharides identified correspond to glucose-derived compounds having undergone several dehydration reactions [14]. The volatile fraction also contains an important amount of furans such as 5-hydroxymethylfurfural (5-HMF), 5-methylfurfural (5-MF), furfural and furfuryl alcohol [12,14,77]. These compounds can also be considered as depolymerization products. Indeed, it has been proven that levoglucosan can be

found not only in pyran form but also in a furan form [10,17], which is more stable [77] and can be obtained by a contraction of the pyran ring. Some furan functional groups are already detected by ^{13}C NMR in the char of cellulose at 270 °C [32]. The contraction of the pyran ring certainly occurs by the rupture of the linkage between the atom of oxygen of the cycle and the atom of carbon C_1, and by a cyclization between the same atom of oxygen and the atom of carbon C_2 [13,33], as illustrated in Fig. 7B. This cyclization can be accompanied by the elimination of some oxygenated groups, leading to the formation of double bonds C=C and thus of furan rings, explaining the observation of these rings in the cellulose char. In some cases, the formation of the furan ring can lead to the rupture of the glycosidic linkages, as in the example presented in Fig. 7C, explaining the releasing of 5-HMF in the volatiles. Then the formation of the other furans frequently identified can be explained by simple mechanisms involving the rupture of relatively weak bonds [13,14,79]. The many reactions of depolymerization also lead to the formation of some unstable compounds containing new functions such as carbonyl and carboxyl groups [29,31]. These compounds undergo dehydration or fragmentation reactions, explaining the high production of H_2O, CO, CO_2 and small chain compounds (hydroxyacetaldehyde, acetaldehyde, hydroxyacetone) on this temperature range [13,25,49].

In cellulose, the amorphous phase is thermally less stable than the very ordered crystalline phase [12]. As a consequence, a decrease in the degree of crystallinity can shift the value of the onset temperature of the conversion, analyzed by TG, to lower value by 20–40 °C [12,80,81]. On the other side, the maximum degradation rate is clearly higher for the celluloses with a high degree of crystallinity. These differences in reactivity also lead to differences in the product yields. The very high depolymerization rate of crystalline cellulose enables the formation of high yields of anhydro-sugars [12,68]. On the contrary, because of its lower stability, some rearrangement reactions such as dehydration and conversion of sugar ring structure happen in the amorphous phase before the high depolymerization [12,78]. Such reactions explain the increase in furan yields obtained by pyrolysis in consequence of treatments applied to decrease the crystallinity of cellulose [12,80]. Moreover the rearrangement reactions give to the residue a higher stability which then limits its depolymerization and results in higher char yields [12,80]. In the study of Zhang et al. [80] the difference in crystallinity of the initial sample can lead to a change in char yield by a factor of 4. Moreover in comparison to the sample with the highest crystallinity, the CO yields obtained by the pyrolysis of the sample with the lowest crystallinity decreased by a factor of 4. As this decrease was balanced by higher CO_2 yields, it appears that decarboxylation reactions are involved in the char formation pathway.

3.2.2.3. Charring process (380–800 °C). From 270 to 400 °C, the structure of the char of cellulose changes drastically. The conversion of the pyran rings is almost complete at 320 °C [32,78]. The concentration of furan rings progressively increases until 350 °C and then decreases [32]. The first benzene rings appear at 300 °C and their concentration in the char becomes preponderant at 400 °C [31,32]. To these benzene rings are linked some remaining aliphatic and oxygenated groups (hydroxyl and ether) [31,32], giving to the cellulose char a structure relatively close to the one of the lignin char at 400 °C. The aliphatic groups progressively disappear between 400 °C and 600 °C [31]. The production of CH_4 in the temperature range 500–600 °C [53,82], simultaneously to the decrease of the concentration of methyl groups in the residue, suggests that CH_4 is produced by a mechanism of demethylation as the one presented in Fig. 5D. In the same manner, the production of CO and H_2 released from the

char of cellulose between 500 °C and 800 °C [49,53,82] certainly happens by mechanisms close to the ones involved during the charring process of lignin (Fig. 5E and F).

3.3. Hemicelluloses conversion

### 3.3.1. Description of hemicelluloses structures

Hemicelluloses are heteropolysaccharides, whose composition varies depending on plant species. Angiosperm hemicelluloses contain mostly xylans, whereas gymnosperm hemicelluloses contain mostly glucomannans [83]. As presented in Fig. 3C, xylans are composed of a linear framework of β-(1→4)-linked β-D-xylopyranose units with branches also containing 4-O-methyl-α-D-glucuronic acid, α-D-glucuronic acid and α-L-arabinofuranose [84,85]. Glucomannans are composed of a linear framework of β-D-glucopyranose and β-D-mannopyranose with β-(1→4)-linkages and branches containing α-D-galactopyranose [17,68] (Fig. 3D). Moreover, in xylans and glucomannans, the units of the main chain are sometimes acetylated in the C_2 or C_3 positions [17,84]. The degree of polymerization of the chains of hemicelluloses is generally lower than 200 and, contrary to the cellulose, the hemicelluloses are only constituted by an amorphous phase [15,85].

3.3.2. Mechanisms of hemicelluloses conversion

Despite the variety in the composition of the hemicelluloses, TG analyses of these constituents show that their conversion mainly occurs in the temperature range 200–350 °C [51,86,87]. Few authors have studied the conversion of a glucomannan extracted from vegetal sources [86]. From the mass loss rate curve, it can be seen that the weight loss is maximum at a temperature close to 310 °C and a shoulder (or a small peak) is present at around 260 °C. More studies have been focused on the conversion of xylan. The mass loss rate curves obtained by the conversion of this latter one, contain two peaks at around 230 and 290 °C [15,25,87], as illustrated in Fig. 8A. Sometimes the peak at 230 °C rather appears as a shoulder of the main peak at 290 °C [28,88]. Regarding the characteristic temperatures of conversion, we can suppose that the conversions of glucomannan and xylan are quite similar with a shift of 20–30 °C. As the highest weight loss is generally associated to the second peak, it suggests that the rapid depolymerization of the main chain (xylopyranose chain in the case of xylan and glucopyranose–mannopyranose chain in the case of glucomannan) occurs at around 290 °C for xylan and 310 °C for glucomannan.

For temperatures higher than 350 °C, the weight loss is associated to the rearrangement of the residue during the charring process [87]. Compared to cellulose, the char yield obtained from the hemicelluloses is higher. This difference is due in part to a catalytic effect of the minerals, in higher content in the hemicelluloses than in the cellulose, which promotes the char formation [24,53]. Moreover, even after the demineralization of the hemicelluloses, the pyrolysis of xylan and glucomannan can give char yields twice and three times higher than with cellulose respectively [16]. This result can be attributed to the difference in thermal stability of the monomer units (or of the linkages between these units) and in the crystallinity of the constituents [17]. As stated during the study of cellulose pyrolysis, before depolymerization, the amorphous phase of a polysaccharide undergoes further rearrangement reactions which promote the char yields, than the crystalline phase.

The main steps of conversion of the hemicelluloses and the volatile compounds released during each step are detailed thereafter and illustrated in Fig. 8B in the case of xylan. The evolution of the chemical structure of the rings is also investigated. For most of
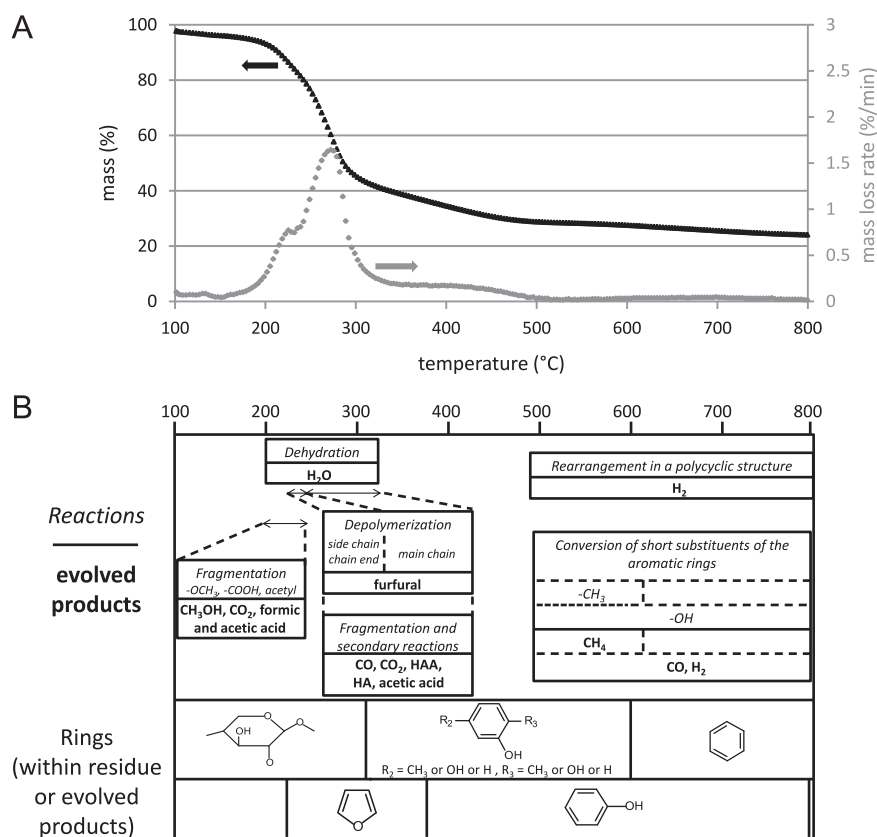
Fig. 8. Xylan pyrolysis: (A) Typical TG analysis (2 °C/min adapted from [23]); and (B) main reactions occuring and evolution of the chemical structures of the rings (within the residue and the evolved products) throughout the temperature increase; HAA: hydroxyacetaldehyde, and HA: hydroxyacetone.

the evolved compounds such as H_2O and CO_2, the curves representing the evolution of their production as a function of the temperature present a similar profile to that of the mass loss rate with two main peaks [25,52]. Particularities observed for some compounds [15,51,89] help to make hypothesis to differentiate the mechanisms associated to these peaks.

3.3.2.1. Dehydration and breaking of less stable linkages (xylan: 150–240 °C, glucomannan: 150–270 °C). The release of H_2O, characteristic of dehydration reactions within the polysaccharides, becomes significant at 200 °C [25,52]. At this temperature, some other chemical functions present in the substituents of the main chains are also unstable. Methanol is produced from the fragmentation of the methoxy group of the 4-O-methyl-α-D-glucuronic acid [15,90]. The rupture of the carboxylic acid function of the hexuronic acids is responsible for the production of formic acid [15]. As acetyl substituents can represent more than 10% in weight of the hemicelluloses, the fragmentation of these groups to produce acetic acid lead to significant yield of this compound [15,87,90]. Regarding xylan conversion, although the weight loss associated to the first peak is lower than the one associated to the second peak, the highest production of methanol, formic acid and acetic acid is simultaneous to the first peak [15,57,89], which suggests that these fragmentation reactions essentially occur at the beginning of the xylan conversion. Some CO_2 molecules are also released from a temperature of 200 °C. Reactions of decarboxylation of the carboxylic acid functions of the hemicelluloses are supposed to be responsible for the formation of these molecules at low temperatures [15,90].

The detection of furfural molecules at temperature as low as 220 °C [15,91] shows that dehydration and fragmentation of some chemical functions are not the only reactions occurring on this temperature range. Indeed, the formation of furan compounds, which are derived compounds of the hexoses and pentoses constituting the hemicelluloses (see next part), proves that some depolymerization reactions are also possible. The depolymerization reactions most likely to happen are the degradation of the side chains and chain-end scission [15,87].

3.3.2.2. Depolymerization (xylan: 240–320 °C, glucomannan: 270–350 °C). With a temperature increase to 240 °C for xylan or 270 °C for glucommanan, the glycosidic linkages between monomer units become very unstable and a rapid depolymerization occurs. These reactions lead to the formation of different anhydro-sugars. In the pyrolysis oil obtained from the conversion of glucomannan, one can find levoglucosan, levomannosan (1,6-anhydro-β-D-mannopyranose) and levogalactosan (1,6-anhydro-α-D-galactopyranose) [16,17,92]. These compounds are formed by the depolymerization of the units of β-D-glucopyranose, β-D-mannopyranose and α-D-galactopyranose respectively, probably following a mechanism similar to the one detailed for the depolymerization of cellulose in levoglucosan (Fig. 7A). As explained above, the pyran rings can be converted to more stable furan rings, explaining the formation of 5-hydroxymethylfurfural, 5-methylfurfural and furfural by depolymerization of glucomannan [16,17,92]. The depolymerization of the β-D-xylopyranose chains of xylan can lead to the formation of 1,4-anhydro-β-D-xylopyranose. But this compound is relatively unstable and was rarely detected in the pyrolysis oil of xylan [15]. Concerning the products containing a

furan ring, only furfural was detected with a significant yield in the pyrolysis oil from xylan [15,87,88]. The fact that the essential of the furan compounds, obtained by the conversion of a polymer constituted by a framework of pentoses, contain 5 atoms of carbon supports the hypothesis that these compounds are essentially formed by a mechanism of depolymerization.

The rapid depolymerization of the hemicelluloses causes the formation of different chemical functions and of many unstable intermediaries. These molecules undergo dehydration, fragmentation and secondary reactions which lead to the formation of significant amount of H_2O, CO_2 and CO [15,25,53]. In addition to anhydro-saccharides and furans, the condensable compounds produced on this temperature range and the most frequently identified are hydroxyacetaldehyde, hydroxyacetone, 1-hydroxy-2-butanone (from xylan), acetic acid and cyclopentenones [16,17,87,88,92].

3.3.2.3. Charring process (xylan: 320–800 °C, glucomannan: 350–800 °C). When temperature increases to more than 300 °C, the structure of the residue becomes more and more aromatic. Some of the benzene rings produced contain methyl or oxygenated substituents, as evidenced by the identification of several methylphenols in the volatiles obtained by the pyrolysis of hemicelluloses at 320 or 350 °C [87,88]. Based on the CH_4 production, which is maximum at a temperature close to 550 °C [52,53,89], it appears that the methyl substituents are converted by a mechanism of demethylation (Fig. 5D) [15]. In the same manner, the production of CO for temperatures higher than 500 °C [15,49] must be due to the rupture of the oxygenated substituents following mechanisms similar to those involved during lignin charring process. Finally the formation of H_2 on the temperature range 480–800 °C is mainly due to dehydrogenation reactions [52,82] during the formation of a more condensed structure (Fig. 5F). Some vapogasification reactions could also be responsible of a production of H_2 [52]. Some reactions occurring during the charring process of the hemicelluloses begin at lower temperatures than for the conversion of lignin and cellulose. For instance, H_2 production is initiated at 480 °C during hemicelluloses conversion against 500 °C for the other constituents. This phenomenon can be explained by a catalytic effect of the minerals [93], present in high content in the hemicelluloses [24,53].

4. Discussion on the influence of biomass composition on pyrolysis yields

4.1. Constituent composition

In order to better understand the mechanisms involved during the pyrolysis of biomass, many authors have firstly studied the individual conversion of each of its main constituents. Despite the difference in composition of lignin, cellulose and hemicelluloses, the pyrolysis of these polymers can be described as the superposition of three main pathways (char formation, depolymerization and fragmentation) and of secondary reactions. The preponderance of the different pathways mainly depends on the temperature of the reactor and of the heating rate of the material. TG analyses are very useful to study the steps of conversion of the particles, but in these works the size of the sample is too small to estimate the yields obtained in large scale reactor. Moreover, in mechanism studies using TG, the heating rate are generally relatively low (< 20 °C/min), what is suitable for char production but far from the conditions required in more recent processes such as fast pyrolysis and gasification. Based on several recent works implemented with higher heating rates (> 100 °C/min), the range of the yields obtained in different kinds of reactors and for

Table 1

Yields (% of dry weight) obtained from individual fast pyrolysis (> 100 °C/min) of the biomass constituents in different types of reactor with temperature between 500 and 800 °C.

	Char	Tar	Water	Gas
Cellulose	< 15	40–70	5–15	12–30
Hemicelluloses	20–30	20–35	20–30	22–35
Lignin	30–45	15–35	8–15	12–35

temperature comprises between 500 and 800 °C are detailed for each constituent in Table 1 [13,16,20,30,94]. The variability in yields ranges is due to differences in conversion parameters but also in the composition of the constituents implemented: proportion of units H, G and S in lignin [27,71], degree of crystallinity of cellulose [12,78,81], proportion and composition of the side chains of the hemicelluloses [15], proportion of glucopyranose and mannopyranose units in the framework of glucomannan [92], etc. For each constituent, the composition of the main products obtained by the different pathways involved in primary mechanisms is summarized in Table 2.

For lignin, the high content of benzene rings which are the moieties forming the char explains the high char yield. As a consequence for the production of a solid fuel which could substitute coal in industrial applications the use of biomass with high lignin content is recommended. On the contrary, in the case of bio-oil production by fast pyrolysis, biomass with low lignin content is preferred. Indeed given the high stability of the benzene rings and of bonds between them, lignin is the main source of high MW compounds called pyrolytic lignin which mainly contribute to the viscosity of the oil [1,22]. Concerning the polysaccharides, the formation of char requires the conversion of the pyran rings and rearrangement reactions which lead in particular to the release of H_2O. Given that the hemicelluloses give much higher yields of char, H_2O and CO_2 than cellulose [25,30], we can suppose that, as in the case of cellulose conversion, some decarboxylation reactions are associated to the rearrangement reactions involved in the char formation of the hemicelluloses. The differences in crystallinity and mineral content are important factors to explain that the hemicelluloses give higher char yields than cellulose. The large yields ranges obtain for the conversion of the cellulose are due to the variability in the crystallinity of the samples. The highest yields of organic condensable compounds are obtained from the samples with high crystallinity. The levoglucosan, which is the main product obtained by cellulose depolymerization, has a potential interest for the production of pharmaceuticals, surfactant and biodegradable polymers [2,95]. The other anhydro-saccharides obtained by the depolymerization of the cellulose and of the hemicelluloses are also a source of chiral auxiliaries useful for the synthesis of drugs or advanced materials [2,44]. The hemicelluloses, especially the xylan, can also give high yields of furfural, which is an organic reagent largely used for the production of medicines, resins and fuel additives [96]. The depolymerization products of lignin are essentially phenolic compounds.

In this study a particular attention has been given to the evolution of the composition of the chemical groups and of the structure of the char. These factors which impact the reactivity and the energy content of the products are critical to determine in which energy application they can be used. Generally biomass is characterized by O/C ratio of 0.7–1 and Higher Heating Value (HHV) of 15–20 MJ/kg [21,97]. Relatively low energy density and other properties of raw biomass (moisture content, fibrous structure) affect process operations and efficiency, and limit its direct use in industrial process as a solid fuel for electricity and heat generation [98,99].

Table 2
Main volatile products obtained by primary mechanisms during the conversion of biomass constituents.

	Char formation		Depolymerization	Fragmentation
	$T < 400\ °C$	$T > 500\ °C$		
Lignin	–	CO, CH$_4$, H$_2$	Guaiacol, catechol, cresol, phenol	Formaldehyde, CO, CO$_2$, acetic acid, CH$_3$OH, CH$_4$
Cellulose	H$_2$O, CO$_2$	CO, CH$_4$, H$_2$	LG, 5-HMF, furfural	CO, CO$_2$, HAA, HA, AA
Hemicelluloses				
Xylan	H$_2$O, CO$_2$	CO, CH$_4$, H$_2$	Furfural	CO$_2$, acetic acid, CH$_3$OH, formic acid, CO, HAA, HA
Glucomannan	H$_2$O, CO$_2$	CO, CH$_4$, H$_2$	LG, levomannosan, furfural	CO$_2$, acetic acid, CO, HAA, HA

LG: levoglucosan, 5-HMF: 5-hydroxymethylfurfural, HAA: hydroxyacetaldehyde, HA: hydroxyacetone, and AA: acetaldehyde.

Torrefaction constitutes a possible option to improve the fuel characteristics of biomass. In this technology in which biomass is treated at temperatures ranging between 200 and 300 °C, only the most unstable oxygenated functions are converted resulting in a decrease of the O/C ratio to around 0.5 [21] and an increase of the HHV (20–25 MJ/kg) [98]. Moreover, torrefaction considerably improves the handling and grinding properties of the material [100]. Such improvements enable to consider the co-feeding of torrefied biomass with coal in combustion and gasification applications [98]. The structure of torrefied biomass is not well ordered explaining its relatively high reactivity in the presence of an oxidizing agent [101].

When char is produced at temperatures higher than 400 °C, pyran and furan rings are converted while the proportion of benzene rings increases. Oxygen is essentially found in the substituents of the benzene rings where the atom is included in ether and hydroxyl groups. Such chars are characterized by O/C ratio inferior to 0.3 [21] and HHV comparable to those of bituminous coal (> 25 MJ/kg) [97,102]. The presence of oxygenated groups is an indicator that the benzene rings are not organized in a highly ordered structure, explaining the high reactivity of biomass char in comparison with coal [101]. Conversion of methoxy group is complete at 500 °C while temperatures higher than 700 °C are required for the degradation of the very stable phenol moiety [4]. It is very interesting to note that, during the charring process ($T > 500$ °C), the compositions of the gaseous compounds released are quite the same for the three constituents (CO, CH$_4$ and H$_2$), which indicates that the structure and the mechanism of conversion of their residues are certainly very similar. Increasing maximum temperature results in rearrangement reactions in a more ordered structure and in a decrease of char reactivity [103].

High stability of the phenol moiety [22], which is also observed in the volatile phase, is a critical issue in fast pyrolysis and gasification applications. Bio-oil produced from biomass fast pyrolysis is a complex mixture of oxygenated compounds. In order to use it for the substitution of conventional liquid fuel, an upgrading step aiming at reducing its oxygen content is necessary [1]. High stability of phenols is known to be a key factor limiting the efficiency of this deoxygenation step [22]. In gasification applications, the presence of tars in relatively high concentration in the produced gas is an indicator of incomplete conversion and limits the development of technologies based on syngas chemistry such as the production of diesel fuel by Fischer–Tropsch synthesis [104]. Phenols are well-known components of these tars which cause several operational problems such as fouling, corrosion and catalyst deactivation [4]. In both applications, in order to convert phenols without implementing very high temperatures ongoing research is focused on the use of catalyst.

4.2. Influence of interactions

Several works have evidenced that an additive law based on the individual conversion of each constituent does not enable to predict precisely the actual yield obtained from lignocellulosic biomass pyrolysis [24–26]. Various interactions have been reported to explain this phenomenon. Within biomass covalent and hydrogen bonds exist between the constituents [105,106]. Such bonds are likely to influence the thermal stability of the polymers and the distribution of the products obtained from their conversion. Moreover, volatiles released from a constituent may react with char formed from another constituent, resulting in additional secondary reactions [24]. In order to estimate the influence of the interactions on yields, the conversion of biomass and a mixture of its constituents physically mixed can be compared [24,107]. However, when studying the pyrolysis of individual or physically mixed constituents, melting phenomenon can be observed [35,54]. As a consequence, changes in yields are not only due to the existence of chemical interactions between constituents but also to difference in heat and mass transfer, ending up in complex result interpretation. Interactions in volatile phase have also been evidenced, in particular during the simultaneous pyrolysis of lignin and cellulose. Hosoya et al. [108] showed that these interactions significantly reduced levoglucosan yield from cellulose while CH$_4$ and catechols from lignin were enhanced at the expense of cresols.

Interactions with inorganic elements present in biomass such as K, Na, Mg and Ca are also frequently reported to influence the conversion [99]. It is well known that secondary reactions such as volatile cracking can be catalyzed at the surface of inorganics and result in higher yields of light compounds [109]. Recent works highlighted that inorganics also influence primary reactions [99,109]. Conversion starting at lower temperature evidences a catalytic effect on matrix reactivity [53,110]. When impregnated in lignin, inorganics catalyze the conversion of methoxy group in methanol [53,111]. In the case of cellulose the presence of inorganic can reduce levoglucosan yield by a factor of 2 or 3 [109]. Another worthwhile result is that inorganics can promote the rearrangement of the aromatic rings which leads to an increase in char [53,110,111] and H$_2$ yields [93,112]. Whatever feedstocks are used, individual constituent [53,110] or biomass sample [11,53], similar evolutions were observed in the presence of inorganics.

5. Conclusion

After a description of the mechanisms involved in the pyrolysis conversion of the polymers constituting biomass, this review gives a comprehensive overview of the steps of conversion of lignin, cellulose and hemicelluloses. This work helps to identify the sources and the pathways involved in the formation of many compounds obtained by the pyrolysis of biomass. In order to guide the conversion to higher yields of specific fuel products, it gives useful information for the selection of the appropriate biomass and of the required conditions. However, the interactions between constituents and the catalytic influence of the minerals naturally

present in biomass can modify significantly the yields of some products and should also be taken into consideration. From these results it appears that for some applications the use of catalyst could enable a better optimization of the conversion and be a decisive option to make thermochemical processes more competitive.

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